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(54) Title: GROWTH OF COLORLESS SILICON CARBIDE CRYSTALS			
(57) Abstract Large single crystals of silicon carbide are grown in a furnace sublimation system. The crystals are grown with compensating levels of p-type and n-type dopants (i.e., roughly equal levels of the two dopants) in order to produce a crystal that is essentially colorless. The crystal may be cut and fashioned into synthetic gemstones having extraordinary toughness and hardness, and a brilliance meeting or exceeding that of diamond.			

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GROWTH OF COLORLESS SILICON CARBIDE CRYSTALS

Field of the Invention

The invention relates to the growth of silicon carbide crystals. More particularly, the invention relates to the growth of transparent, 5 monocrystalline, colorless silicon carbide crystals. Because of their durability and other advantageous physical and crystal properties, these crystals may be cut and fashioned into finished gemstones having the fire and brilliance of diamond.

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Background of the Invention

Silicon carbide (SiC) is rarely found in nature. It has, however, been manufactured for more than eighty years, in crystalline form, for abrasive products. Silicon carbide crystals found in nature and 15 in abrasive products are generally black and not translucent because they contain substantial levels of impurity atoms.

Because of the theoretically quite favorable electronic properties of silicon carbide, significant 20 development activities were initiated during the 1960s and 1970s with the objective of growing large (bulk) crystals of low impurity silicon carbide for use in the production of semiconductor devices. These efforts finally resulted in the commercial availability of 25 relatively low impurity, translucent silicon carbide crystals. These silicon carbide crystals are fabricated and marketed as very thin, green, amber or blue (175 μ m - 400 μ m) slices useful for semiconductor devices.

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Recently, it has been discovered that relatively low impurity, translucent, single crystal silicon carbide may be grown with a desired color and thereafter cut and fashioned into synthetic gemstones.

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These gemstones have extraordinary hardness, toughness, chemical and thermal stability, and a high refractive index that produces unparalleled brilliance. The single crystals from which the gemstones are produced 5 have been grown by sublimation according to techniques of the type described in U.S. patent number Re. 34,061.

Silicon carbide crystals can be grown in a wide range of colors (including green, blue, red, purple, yellow, amber and black) and shades within each 10 color by the appropriate selection of dopants (e.g., nitrogen and aluminum) and by varying the net doping densities (concentrations). Because of its wide bandgap, undoped ("intrinsic") silicon carbide crystals in the hexagonal or rhombohedral forms are inherently 15 colorless. Thus, silicon carbide crystals offer the potential to be cut and fashioned into gemstones of many various appearances, including that of diamond.

Although the colored crystals have proven relatively easy to produce, problems have been 20 encountered in creating the exceedingly impurity-free sublimation system environment necessary for growing undoped, colorless silicon carbide. Because colorless silicon carbide gemstones have an extraordinary appeal, there is a need for a more cost effective and reliable 25 process for growing large single crystals of silicon carbide in colorless form.

Summary of the Invention

The present invention, in one broad aspect, is the discovery that large, transparent, colorless 30 silicon carbide crystals may be grown in a sublimation system where compensating levels of n-type and p-type dopants are introduced into the crystals's lattice structure. The compensated levels of p-type and n-type dopants (i.e., roughly equal levels of the two dopants) 35 serve to produce a colorless crystal by canceling each other in terms of the production of color centers in

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the crystal. The compensation is best carried out at low carrier levels. For example, the preferred n-type dopant, nitrogen, may be introduced into the lattice only at those low levels dictated by "background" 5 atmospheric nitrogen present in the sublimation system. A like amount of p-type dopant, e.g., aluminum, may be introduced via the sublimation powder or gas at a level sufficient to compensate for the background level of nitrogen. Thus, in one aspect, the present invention 10 may be described as a colorless single crystal of silicon carbide grown with compensated levels of n-type and p-type dopants. These crystals may be cut and fashioned into brilliant colorless synthetic gemstones.

In another aspect, the invention may be 15 defined as a method of producing a colorless single crystal of silicon carbide comprising the step of growing the single crystal of silicon carbide by a sublimation technique wherein compensated levels of p-type and n-type dopants are introduced into the crystal 20 lattice structure.

Detailed Description of the Invention

It is to be understood at the outset of the description which follows that persons of skill in the appropriate arts may modify the invention as herein 25 described while still achieving the favorable results of this invention. Accordingly, the description which follows is to be understood as being a broad, teaching disclosure directed to persons of skill in the appropriate arts, and not as limited upon the present 30 invention.

Additionally, a number of the definitions, techniques and other aspects in the field of natural and synthetic gems and gemstones are well known to those of ordinary skill in this art. Relevant 35 background and related information can be found, for example, in Volume 7 of the McGraw-Hill Encyclopedia of

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Science & Technology, 7th Ed. (1992) at pages 651-659. It will be understood, of course, that this source is exemplary of the general knowledge in this art, rather than any limitation of the present invention.

5 In a preferred manner of practicing the invention, the growth of large, colorless single crystals of silicon carbide is achieved by introducing a polished monocrystalline seed crystal of silicon carbide of a desired polytype into the furnace of a
10 sublimation system along with silicon and carbon containing source gas or powder (source material). The source material is heated to a temperature that causes the source material to create a vapor flux that deposits vaporized Si, Si₂C, and SiC₂, to the growth
15 surface of the seed crystal. The reproducible growth of a single selected polytype on the seed crystal is achieved by maintaining a constant flux of Si, Si₂C and SiC₂, and controlling the thermal gradient between the source material and the seed crystal. The growth
20 procedure described above is set forth in more detail in U.S. patent number Re. 34,861, the teachings of which are incorporated entirely herein by reference.

25 During the growth process of the present invention, roughly equal amounts of p-type and n-type dopants are maintained in the atmosphere of the sublimation furnace so that compensated levels of these two dopant types are introduced into the crystal lattice structure. In one preferred embodiment, the n-type dopant is nitrogen. The nitrogen source is the
30 nitrogen present in the furnace atmosphere at "background" levels. Therefore, according to this embodiment, a p-type dopant, preferably aluminum, is added to the source powder in an appropriate amount so that the nitrogen and aluminum are incorporated into
35 the crystal lattice structure in compensated amounts. In this regard, "compensated," "compensated amount," "compensated level," and like terms, are used to refer

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to those roughly equal levels of p-type and n-type dopant atoms incorporated into the silicon carbide crystal lattice structure whereby the crystal is rendered essentially colorless.

5 In this regard, the terms "compensation" or "compensated" are also used in describing the electronic properties of a crystal, and likewise describes a semiconductor material that contains (frequently intentionally) both p and n-type dopants, 10 including material in which one or the other predominates; e.g. a "compensated p-type material." Also, some uses refer to material in which p or n predominate as being "overcompensated" rather than simply "compensated." Thus, the terms "compensated" 15 and "overcompensated" are familiar to those of ordinary skill in the semiconductor field.

It has been found desirable to compensate p-type and n-type dopants at low carrier levels. Thus, prior to initiating the sublimation growth process, the 20 background level of atmospheric nitrogen in the furnace is desirably reduced to a relatively low level, for example, a level that will generally create an n-type dopant level in the crystal lattice on the order of about 1×10^{16} to 1×10^{18} atoms/cubic centimeter (cm^{-3}) 25 with a more preferred range being between about 1×10^{17} cm^{-3} x 5 to 10^{17} cm^{-3} . Reducing the level of atmospheric nitrogen in the furnace can be achieved by methods known in the art, typically, by backfilling with an inert gas such as argon, following by evacuating the 30 furnace to very low pressure.

The compensated level of the p-type dopant is not absolutely critical provided it produces a crystal having sufficient colorless properties for the intended end use. Thus, broadly stated, the invention 35 encompasses compensation that meets this goal, whether the dopant density is greater for the p-type or n-type dopant. It has been found desirable, however,

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especially where the n-type dopant is nitrogen and the p-type dopant is aluminum, to have a greater density of aluminum atoms in the crystal lattice. Thus, in a preferred manner of practicing the invention, the level 5 of aluminum atoms is in the range of one to five times that of the nitrogen atoms, with a more preferred range being one to two times.

The reasons for a somewhat greater density of p-type aluminum atoms are two-fold. First, p-type 10 aluminum doping alone tends to impart a blue color to silicon carbide crystals, while n-type nitrogen doping alone tends to impart a green or amber color. Because colorless brilliance for gemstone applications is desired, a slight blue tint is preferable to a slight 15 green or amber tint. Generally speaking, the preference arises from the aesthetic viewpoint that a blue tint is less detrimental than some other tint and, in some cases, is deemed desirable. The second reason for erring on the side of aluminum overcompensation is 20 that aluminum is a deeper level dopant than nitrogen. Thus, at room temperature, the crystal will contain fewer active carriers due to an overcompensation of nitrogen. Because active carrier concentration is directly linked to the creation of color centers within 25 the crystal, an overcompensation of aluminum is more likely to reduce the color of the crystal than will an overcompensation of nitrogen.

It will be appreciated that other dopants may be used, and that the dopants may be used at other 30 densities. For example, the p-type dopant may be boron or beryllium, or other Group I, II or III elements. Similarly, other Group V elements may be used as n-type dopants in silicon carbide.

The present invention may be utilized to grow 35 colorless crystals of different polytypes. In this regard, silicon carbide is a complex material system that forms more than 150 different polytypes, each

having different physical and electronic properties. The different polytypes can be classified in three basic terms: cubic, rhombohedral and hexagonal. Both the rhombohedral and hexagonal forms can occur in a 5 number of different atomic arrangements that vary according to atomic stacking sequence. According to the invention, the preferred polytypes are 2H, 6H, 4H, 8H, 15R and 3C.

Large, colorless single crystals of silicon 10 carbide grown by the techniques described above are ideally suited for use as gemstone materials. The colorless single crystals, if large enough, are first cut into a number of smaller pieces that serve as the rough gemstone material. The rough gemstones 15 thereafter may be fashioned into finished gemstones by utilizing equipment currently employed in the art for fashioning diamonds and natural colored gemstones. Preferably, the silicon carbide gemstones of the 20 invention are fashioned with precision diamond cuts to take advantage of the extraordinarily high refractive index of the silicon carbide material.

As noted earlier, those techniques required to turn an appropriate material into a final gemstone 25 are generally well understood, and can be applied to the silicon carbide material of the present invention without undue experimentation.

Although the invention has been described in connection with certain embodiments, it will be appreciated that modifications may be made without 30 departing from the true spirit and scope of the invention.

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THAT WHICH IS CLAIMED IS:

1. A synthetic gemstone formed from a colorless, single crystal of silicon carbide containing compensated levels of n-type and p-type dopants.
2. A synthetic gemstone as claimed in Claim 1 wherein the n-type dopant comprises nitrogen.
3. A synthetic gemstone as claimed in Claim 2 wherein nitrogen atoms are present in the crystal at a concentration dictated by background levels of nitrogen in the sublimation system.
- 10 4. A synthetic gemstone as claimed in Claim 2 wherein the n-type dopant comprises aluminum.
5. A synthetic gemstone as claimed in Claim 4 wherein the concentration of aluminum atoms is in the range of about one to five times that of nitrogen atoms.
- 15 6. A synthetic gemstone as claimed in Claim 4 wherein the concentration of aluminum atoms is between about one and two times the concentration of nitrogen atoms.
- 20 7. A colorless single crystal of silicon carbide grown with compensated levels of n-type and p-type dopants.
- 25 8. A synthetic gemstone according to Claim 7 or Claim 10 wherein the polytype of the silicon carbide single crystal is selected from the group consisting of 2H, 6H, 4H, 8H, 15R and 3C.

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9. A colorless single crystal of silicon carbide according to Claim 1 or Claim 7 wherein each dopant type is present in the crystal at a concentration of between about $1 \times 10^{16} \text{ cm}^{-3}$ and $1 \times 10^{18} \text{ cm}^{-3}$.

10. A colorless single crystal of silicon carbide according to Claim 1 or Claim 7 wherein each dopant type is present in the crystal at a concentration of between about $1 \times 10^{17} \text{ cm}^{-3}$ and $5 \times 10^{17} \text{ cm}^{-3}$.

11. A colorless single crystal of silicon carbide as claimed in Claim 9 wherein the n-type dopant comprises nitrogen and the p-type dopant comprises aluminum.

15 12. A method of producing a colorless single crystal of silicon carbide comprising growing the single crystal of silicon carbide by a sublimation technique while introducing compensated levels of p-type and n-type dopants into the crystal lattice 20 structure.

13. A method as claimed in Claim 12 wherein the n-type dopant comprises nitrogen and the sublimation technique incorporates a furnace having an atmosphere containing nitrogen only at background 25 levels, and including the step of introducing the p-type dopant at a compensated level roughly equivalent to the amount of nitrogen introduced into the crystal due to the atmospheric background presence of nitrogen.

14. A method as claimed in Claim 13. wherein 30 the p-type dopant comprises aluminum and including the step of introducing aluminum atoms into the crystal lattice structure at a concentration from about one to

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five times the concentration of nitrogen atoms in the lattice structure.

15. A method as claimed in Claim 13 wherein the p-type dopant comprises aluminum and including the 5 step of introducing aluminum atoms into the crystal lattice structure at a concentration from about one to two times the concentration of nitrogen atoms in the lattice structure.

16. A method as claimed in Claim 12 wherein 10 each dopant type is present in the crystal at a concentration of between about $1 \times 10^{16} \text{ cm}^{-3}$ and $1 \times 10^{18} \text{ cm}^{-3}$.

17. A method as claimed in Claim 14 wherein 15 each dopant type is present in the crystal at a concentration of between about $1 \times 10^{17} \text{ cm}^{-3}$ and $5 \times 10^{17} \text{ cm}^{-3}$.

18. A method according to Claim 12 wherein the sublimation technique comprises:

introducing a monocrystalline seed crystal of 20 silicon carbide of desired polytype and a silicon carbide source powder into a sublimation system;

raising the temperature of the silicon carbide source powder to a temperature sufficient for the source powder to sublime; while

25 elevating the temperature of the growth surface of the seed crystal to a temperature approaching the temperature of the source powder, but lower than the temperature of the source powder and lower than that at which silicon carbide will sublime 30 under the gas pressure conditions of the sublimation system; and

generating and maintaining a substantially constant flow of vaporized Si, Si₂C, and SiC₂ per unit

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area per unit time from the source powder to the growth surface of the seed crystal for a time sufficient to produce a desired amount of macroscopic growth of monocrystalline silicon carbide of desired polytype 5 upon the seed crystal; and maintaining levels of p-type and n-type dopant atoms in the sublimation system sufficient to introduce compensated levels of the two dopant types into the crystal lattice structure.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/01292

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C30B23/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C30B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>JOURNAL OF CRYSTAL GROWTH, vol. 115, no. 1 / 04, 2 December 1991, pages 733-739, XP000322885</p> <p>WOO SIK YOO ET AL: "BULK CRYSTAL GROWTH OF 6H-SiC ON POLYTYPE-CONTROLLED SUBSTRATES THROUGH VAPOR PHASE AND CHARACTERIZATION" see page 735, right-hand column see page 736, right-hand column see page 737, left-hand column ---</p>	1-4,7,8, 12
A	<p>US RE34861 E (DAVIS ROBERT F ET AL) 14 February 1995 see claim 1 -----</p>	18

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

...information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US RE34861 E	14-02-95	US 4866005 A	12-09-89
		CA 1331730 A	30-08-94
		DE 3855539 D	17-10-96
		DE 3855539 T	23-01-97
		EP 0389533 A	03-10-90
		EP 0712150 A	15-05-96
		JP 3501118 T	14-03-91
		WO 8904055 A	05-05-89